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SIMULTANEOUS POLYMERIZATION AND CRYSTALLIZATION: A NEW METHOD FO--ETC(U)  
AUG 78 B M FOXMAN, S W GERSTEN  
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<sup>6</sup> Simultaneous Polymerization and Crystallization: A New Method  
for the Preparation of Mixed-metal Coordination Polymers.

<sup>10</sup> Bruce M. Foxman and Susan W. Gersten

Department of Chemistry

Brandeis University

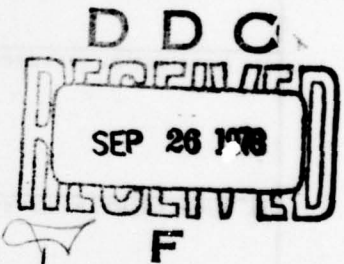
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The usefulness of simultaneous polymerization and crystallization as a preparative tool for transition metal polymers is established; syntheses of both stable and metastable mixed-metal (M=Ni,Co) polymers are described. The metastable polymers show solid-state reactivity as well as room-temperature photochromism.		

Simultaneous Polymerization and Crystallization: A New Method  
for the Preparation of Mixed-metal Coordination Polymers

by Bruce M. Foxman\* and Susan W. Gersten

(Department of Chemistry, Brandeis University, Waltham, MA 02154)

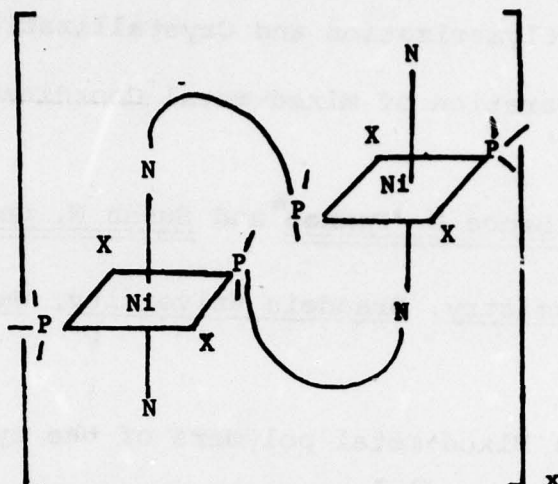
Summary: Mixed-metal polymers of the type  $\{ \text{Ni}_{0.5} \text{Co}_{0.5} \text{Cl}_2 [\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3]_2 \}_x$  have been prepared under various conditions; the low-temperature products have unusual properties, e.g. photochromism, and may be converted to the high temperature form in the solid state.

The preparation of solid, crystalline polymers has been reviewed recently.<sup>1</sup> However, the current technology has not often been applied in inorganic chemistry, e.g., to the production of transition-metal coordination polymers. We have previously demonstrated the high crystallographic and chemical specificity of a solid-state reaction leading to such polymers,<sup>2</sup> and report here the synthesis of mixed-metal polymers via simultaneous polymerization and crystallization.<sup>3</sup> The synthesis of polymeric  $\text{NiX}_2\text{L}_2$  (where  $\text{X} = \text{Cl}, \text{Br}$ ;  $\text{L} = \text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$ ) has previously been reported by solid-state or solution techniques, and the complex has been shown to have the structure<sup>2,4,5</sup>

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The mixed-metal polymer,  $[\text{Ni}_{0.5}\text{Co}_{0.5}\text{Cl}_2\text{L}_2]_x$ , may be prepared at ambient temperature by the reaction of equimolar amounts<sup>6</sup> of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  with an excess of L in an ethanol-acetone-triethylorthoformate (6:5:1) solution. A red precipitate [ $\text{NiCl}_2\text{L}_2$  monomer, square planar] appears immediately in the purple solution. Solvent is then allowed to evaporate slowly; after loss of about 80% of the solvent, the  $\text{NiCl}_2\text{L}_2$  monomer dissolves, and crystalline product forms rapidly, leaving a clear solution. In a typical preparation, three products are obtained: purple (~ 90%), green (~ 8%) and yellow (~2%) crystals. When the same reaction is carried out under reflux, a single product, deep blue in color, is obtained.

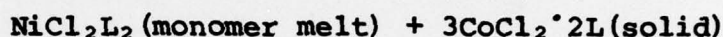
The low temperature preparation is rather unusual in that  $3\text{CoCl}_2 \cdot 2\text{L}$ , which is believed to have a trimeric cage structure of tetrahedrally coordinated Co(II),<sup>5</sup> does not form.  $3\text{CoCl}_2 \cdot 2\text{L}$  is an exceptionally stable, intractable blue solid, which precipitates immediately upon addition of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  to an acetone

solution of L.

The mixed-metal polymer is characterized by the following properties:

(i) Upon rapid heating of the low temperature product the following color changes are observed:

Purple ( $\mu=3.94$ ), green or yellow  $\xrightarrow{146^\circ \text{ C}}$  deep blue ( $\mu=3.71$ )  $\xrightarrow{170^\circ \text{ C}}$



Although the low-temperature materials transform rapidly and irreversibly at  $146^\circ$  to the deep blue form of the polymer, they are stable for 6-12 months at room temperature.

(ii) The purple crystals exhibit photochromic behavior. White-light irradiation causes the purple color to fade to a pale blue; if the light source is removed, the color returns to purple.

The yellow and green polymers are not photochromic.

(iii) All four species are crystallographically identical and are isomorphous with the pure nickel polymer,  $[\text{NiX}_2\text{L}_2]_x^{2,4}$ .

However, differential scanning calorimetry indicates an endothermic change at  $\sim 146^\circ$ , corresponding, e.g., to the purple  $\rightarrow$  deep blue color change. The exact explanation for the various colors is unclear, but may involve "lattice strain", which shows some similar characteristics.<sup>7</sup>

In conclusion, we have found a useful method for the preparation of metastable coordination polymers with unusual properties. As pointed out by Wunderlich,<sup>3b</sup> one can expect perfect coupling of polymerization and crystallization near the ceiling temperature for that process, leading to unlimited size, perfection and molecular weight for a polymer. In the event that the simultaneous polymerization and crystallization occur far from the ceiling temperature, imperfect metastable crystals may result. Clearly, the former set of conditions apply to the high-temperature polymerization and the latter to the low-temperature process. These principles together with the experiments described herein suggest that simultaneous polymerization and crystallization techniques may have general utility for the production of both stable and metastable mixed-metal coordination polymers.

This work was supported in part by the Office of Naval Research.



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